METHOD FOR REUSING FERROUS SCRAP

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Abstract

PURPOSE:To effecvely use iron scrap by oxidizing the ferrous scrap with steam at the specific temp., producing hydrogen gas and separating and recovering difficult-to-oxidizing non-ferrous metals from the scrap already raising temp.

CONSTITUTION:The iron scrap 1 as desmantled automotive scrap, etc., is cut with a shredder, etc., and its temp. is raised and the scrap is charged into a solid layer type reaction vessel lining Al_2O_3 series refractory 5 and having a high frequency coil 6. While blowing N_2 gas from tuyeres 4, the scrap is heated at about 900-1000 deg.C with the coil 6 and blowing gas changes to the steam 2. Therefore, mixed gas 3 of the hydrogen and the steam is produced and iron oxide and difficult-to-oxidizing non-ferrous metals (Cu, Ni, Sn, etc.) are remained. This residue is finely pulverized and separating treatment is executed with magnetic separation, sp. gr. separation, etc., and the iron oxide and non-oxidizing Cu, Ni, Sn, etc., are separately recovered.

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Recycling Method of Fe-base Metal Scraps

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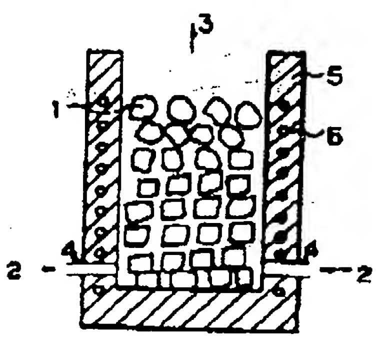
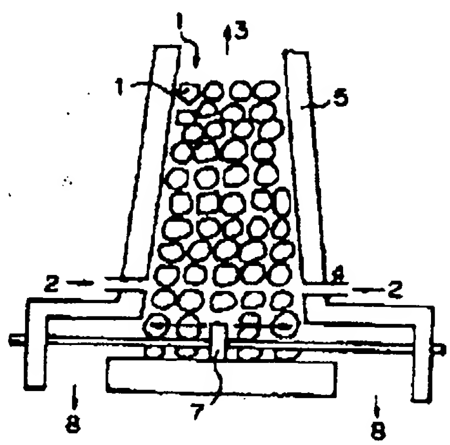
Name of Invention

Recycling Method of Fe-base Metal Scraps





Summary

1. Objective

The objective of this invention is to effectively recycle *Fe-base metal scraps, such as dismantled automotive metal scraps, as a resource.

(Translator's Note: Fe-base metal scraps = scrap metals in which iron or steel is the primary content)

2. Components

This invention makes it possible to produce hydrogen and recover nonferrous metals such as copper, nickel, and tin from Fe-base metal scraps. The scraps are oxidized with steam which is above 700°C in temperature to produce hydrogen. Nonferrous metals, which are hard to oxidize, are then separated and recovered from the scraps.

Scope of Patent Claims

Claim 1:

This invention concerns a recycling method with which Fe-base metal scraps, such as dismantled automotive metal scraps, are steamed at a temperature above 700°C and oxidized to produce hydrogen, and then recover various metals from those already processed scrap metals.

Claim 2:

In the recycling method described in Claim 1, a counterflow reactor, such as a shaft furnace, is used.

Claim 3:

In the recycling method described in Claim 1, the said Fe-base metal scraps are screened and sized by a cutting machine, such as a shredder.

Claim 4:

In the recycling method described in Claim 1, the processed metal scraps are put through a crusher to separate iron oxide, copper, nickel, and tin as a raw metal source.

Detailed Description of Invention

Industrial Application

This invention concerns the recycling of Fe-base metal scraps, such as dismantled automotive metal scraps. This invention makes it possible to effectively recycle metal scraps as a reusable resource. Specifically, the Fe-base metal scraps containing other nonferrous metals, whose direct recycling is very difficult, are used to produce a clean energy, hydrogen, and recover nonferrous metals such as copper, nickel, and tin.

Conventional Technology

In a conventional recycling method, after Fe-base metal scraps are collected and sorted, they are sized by a cutting machine called a "guillotine" or by a shredder. During this process nonmetals, such as rubber and plastic, and nonferrous metals, such as copper and the like, are also removed from the metal scraps so as to be reused for steel production. But, it is difficult to isolate and remove nonferrous (Cu, Sn, etc.) metal parts, such as small motors used in cars and home appli-

ances, from the metal scraps.

As a result, these Fe-base metal scraps are usually melted in an electric furnace and made into round bars which do not have to meet the stringent impurity control on Cu, Sn, etc. Due to the fact that these nonferrous metals (also referred to as the tramp elements), such as Cu, Sn, and the like, contained in the Fe-base metal scraps can be problematic in the hot and cold rolling processes, only a very small amount of these scraps are used at blast furnace steel mills for the production of steel sheets, plates, and pipes.

While the technological know-how to remove certain impurities, such as S, P, O, N, and C, has been well established in steel refinery, there is not yet a perfected technique to remove tramp elements, such as Cu, Sn, etc. Only in a laboratory level, ultra vacuum or ultra high temperature to vaporize the tramp elements, and sulfuric compounds as a flux are tested. These methods have technical problems and are not economically feasible. Much like the western countries, Japan is facing the increase of Fe-base metal scraps in recent years. Currently, approximately 22 million tons of scraps are generated annually, mostly from construction, machinery, automobiles, home appliances, etc. This quantity is expected to almost double by 2020.

On the other hand, more and more steel products are expected to be added with high value, such as surface treatment or cladding. Since the scraps from these products will contain a lot of impurities, it would be difficult to directly reuse them for steelmaking. Also it is assumed that in order not to contribute to global warming, a kind of metal scrap which generate less CO_2 gas will be preferred in refinery. Therefore it would be a major challenge in the future to produce not only round bars but also other steel products using Fe-base metal scraps which are constantly increasing.

Challenges

The reason why it's so difficult to remove these tramp elements (Cu, Sn, etc.) in the refining process is because they do not oxidize as easily as iron does. In other words, once all the available iron gets oxidized these tramp elements can be easily separated. But, there is not much merit if the scrap metals are oxidized with air or oxygen and simply turned into iron oxide .

On the other hand, hydrogen is recognized as a clean energy and thus its demand is expected to increase in oil refinery and ammonia synthesis. Hydrogen is produced from natural or petroleum gases which contain as a main component hydrocarbon gases, such as methane, propane, etc. Those gases are first converted into CO and H_2 (or hydrogen) using steam. Then they are further

changed into carbon dioxide and hydrogen using the "watershift reaction", and then carbon dioxide is separated and removed to isolated hydrogen. But the above method does not contribute to the conservation of natural resources and the reduction of CO_2 emissions. When it comes to counter-measures to deal with global warming, both of them are likely to become a concern in the future.

The ideal method is to produce hydrogen from water using solar or other clean energy, but at the moment it is not yet feasible both technically and economically. Therefore, the objective of this invention is to provide a method with which, while successfully removing tramp elements, hydrogen is produced from Fe-base metal scraps without CO_2 emissions.

Resolutions

The inventors of this invention have made the findings described below.

(1) Scrap metals can be considered as an energy source and converted into hydrogen using steam.

$$Fe + H_2O = FeO + H_2 \quad \text{or} \quad Fe + 4/3\ H_2O = 1/3\ Fe_3O_4 + 4/3\ H_2$$

The above chemical equations are both exothermic reactions and it's possible to produce these reactions with no or little additional thermal energy depending upon the thermal efficiency of the reactor used.

(2) The impurities in the scrap metals such as Cu, Sn, etc. are found in small motors and the like and do not oxidize with steam. But after being fully oxidized with steam the scraps can become very brittle and crushed thoroughly. As a result, the impurities can be easily separated and removed using the magnetic or gravity separation process. Since the recovered iron oxide contains virtually no tramp elements, it can be used in steelmaking with no problem.

This invention concerns the recycling of Fe-base metal scraps such as dismantled automotive scraps. These scraps are steamed at a temperature above 700°C and oxidized to produce hydrogen gas. Those oxidized scraps are then recovered for steelmaking. The counterflow reactor such as a shaft furnace can be used for the steam oxidization to optimize the merit of this invention. The said Fe-base metal scraps can be sized and sorted through the cutting process using a shredder or the like before they are recycled in this invention.

After the scraps processed in the said method are crushed, nonferrous metals such as Cu, Ni, Sn, and the like are separated and recovered, and remaining iron oxide can be recycled in steelmaking.

This invention allows for the recycling of the resources. The Fe-base metal scraps are steamed at a temperature above 700°C and oxidized to produce hydrogen gas. The contained nonferrous metals, such as Cu, Ni, Sn, and the like, are separated and removed. While this invention works with any kind of Fe-base metal scraps ranging from dismantled automotive scraps to home appliances to machine and building scraps, it can be most beneficial when the scraps contain nonferrous tramp elements.

Steam oxidation process, in which iron is oxidized with steam to produce hydrogen, has been known to be a method to produce hydrogen. But this method is only for hydrogen production and uses reduced iron ore. When iron ore is oxidized, it is used after being reduced again.
Compared with this conventional method, the iron oxide created from Fe-base metal scraps by the steam oxidation process of this invention is found to be very brittle and rich in magnetite. This invention is based upon a combination of these facts and a method to process Fe-base metal scraps, particularly the scraps containing nonferrous metals from which it has been thought to be too difficult to recover iron oxide. The conception of this invention is quite unique in the way that all these beneficial facts are assembled together to achieve an economically feasible way to separate and recover metal resources.

Effect

The reason why the process conditions in this invention are defined as described above is explained here. Steam injected into the furnace is heated above 700°C so as to assure a thorough reaction between scraps and steam. In order to achieve such high temperature, it is necessary to either preheat the scraps in some way before feeding them into the furnace or to inject hot inert gas into the furnace to preheat the scraps.

Figure 1 is a graph showing the oxidized layer thickness of 30 mm thick sheet iron after being oxidized with steam for 20 hours. It indicates a very slow reaction, but the dense layer of iron oxide was formed. This reaction can be accelerated as the temperature inside the furnace goes up. Most of the shredded scraps are sheet iron shreds which are approximately 1 mm thick and lightly pressed. Therefore, when the metal scraps are to stay inside the furnace for a maximum of 20 hours and both surfaces of sheet iron scraps are to be oxidized, it is necessary to maintain a temperature above 700°C to oxidize 70% of scraps or 7 mm (0.35 mm each surface) of 1 mm thick sheet iron. By the way, it takes 70 hours to oxidize 70% of the same amount of scraps when 600°C steam is applied.

The reason why a counterflow-bed furnace is used as a reactor is because it enhances the heat

exchange and reaction between solids (or scraps) and gas resulting in improving thermal efficiency of the whole process. As a counterflow-bed furnace, a shaft furnace, a rotary kiln, or a grate kiln can be cited. A fixed-bed furnace is less effective than the above counterflow-bed furnaces in terms of the thermal efficiency, but it can still be used (for this invention). It is recommended that the metal scraps be shredded and sized so that the gas flow can be relatively even inside the furnace. This also adds a handling convenience. It is recommended that the metal scraps be put through magnetic separation to roughly sort nonmetallic elements such as rubber and plastic before being fed into a shredder. When those nonmetallic elements are burned, they produce CO, CO_2, and N_2 gases which will complicate the process to recover hydrogen gas.

When iron gets oxidized, it loses most of its elasticity, ductility, and strength. As a result it can be crushed with little force. The magnetite (Fe_3O_4) produced in this process is magnetic and its specific gravity is approximately 5.2. On the other hand, nonferrous metals, such as Cu, Ni, and Sn, are not easily oxidized. Their specific gravities are 8.96, 8.9, and 7.30 respectively. These nonferrous metals remain intact, for they do not get oxidized. They are not magnetic and are lighter than iron oxide in terms of specific gravity. This makes it easy to separate and recover these metals using the magnetic or gravity separation. The steam oxidization process of this invention can turn the iron content in the scraps into iron oxide. The scraps are then crushed into pieces fine enough for iron oxide and nonferrous metals to be separated. Then with the magnetic and gravity separations, iron oxide is recovered as a good source for raw iron due to its low content of tramp elements and nonferrous metals as sources of raw copper, nickel, and tin.

Demonstration 1

In this demonstration, a small fixed-bed reactor (or furnace) was used as shown in Figure 2. Metal scraps were oxidized with steam and hydrogen was produced and recovered. As shown Figure 2, 150 kg of shredded scraps were fed into the furnace. This fixed-bed furnace was equipped with a high-frequency coil to generate heat, and its interior surface was covered with A1203-type refractory lining. The furnace was 400 mm in inner diameter and 1500 mm in height. N_2 gas was introduced through two tuyeres to heat the furnace. After the furnace temperature reached 900°C or 1000°C, N_2 gas was replaced with steam. The steam was injected for 3 hours at 900°C and 2 hours at 1000°C. The flow rate of steam was set at 120 Nm^3/hr.

A mixture of steam and hydrogen gas produced in this process was measured for flow rate and analyzed for composition after being cooled and filtered for dust. The processed scraps were removed from the furnace and analyzed after they were cooled with N_2 gas through the tuyeres. The

mixture of steam and hydrogen gas generated in the process was then cooled to separate steam. Since all the steam in the mixture turned to water, the remaining gas was virtually 100% hydrogen. The amount of hydrogen gas was totaled to be $76Nm^3$ at 1000°C and $54Nm^3$ at 900°C.

The processed scraps were analyzed for magnetite content. At 1000°C approximately 95% and at 900°C 75% of the scrap metals were oxidized to become magnetite. While small motors were contained in the metal scraps, the copper used in the motors remained intact (or unchanged). This demonstration has proved that: it is possible to produce hydrogen by oxidizing metal scraps with steam, and this can be achieved in a relatively short time when the scraps consist of sheet metals which are shredded and pressed.

Demonstration 2

In this demonstration, a shaft-furnace counterflow reactor was tested for continuous operation as shown in Figure 3. 1.6 ton of shredded scrap metals were fed into the furnace. The interior surface of this shaft furnace was covered with A1203-type refractory lining. The furnace was 800 mm in inner diameter and 3000 mm in height. Hot N_2 gas, which was heated at 1000°C, was introduced through the tuyeres to preheat the scraps up to 800°C. Later when N_2 gas was replaced with steam, a continuous operation was started by feeding metal scraps into the furnace while removing part of the processed scraps from the discharge opening at the bottom of the furnace by a scraper. The operation reached a steady state after approximately 4 hours of operation and was continued for approximately 20 hours afterward.

The discharge velocity was set at about 0.4 ton/hr. and the steam injection rate of about $430Nm^3$/hr. The gas discharge rate at the top of the furnace was about $430Nm^3$/hr and its composition was approximately 48% hydrogen and 52% water. The analysis on the processed scraps revealed that approximately 95% of all the scrap iron was oxidized to become magnetite. The temperature of discharged scraps was about 400°C.

The scraps inside the furnace were 2.8 m high and the core temperature of the scraps was 950 ~ 1050°C. The core was about 0.7 m ~ 2.4 m wide. This high temperature at the core was due to the exothermic reaction of the oxidation of iron by steam. This demonstration has proved that it is possible to produce hydrogen by oxidizing metal scraps with steam in high thermal efficiency. The copper content in the scraps remained intact as copper all through this oxidation-with-steam process.

Demonstration 3

The scraps which were processed in Demonstration 2 were crushed to 5 ~ 30 mm in size. The crushed scraps were put through the gravity separation using a centrifugal force and then the magnetic separation, so as to separate them into two parts, one with magnetite as a primary content and the other with nonferrous metals such as Cu, Ni, Sn, etc. This separation process was done with no difficulty due to the fact that the crushed scraps consisted mostly of magnetite. Before this steam oxidation process, approximately 0.30% copper, 0.07% nickel, and 0.018% tin were found as the tramp elements in the metal scraps. The part with magnetite as a primary content was found to contain 0.02% copper, 0.01% nickel, and 0.005% tin.

Therefore, when the scrap metals after being processed in this invention are crushed and their tramp elements are removed through gravity and magnetic separations, they can be recycled for steelmaking.

Effect of Invention

This invention enables the production of hydrogen gas from metal scraps which contain tramp elements such as copper, nickel, tin, etc. and are thus very difficult to be recycled for steelmaking. The scraps, after having gone through the steam oxidation process in this invention, are crushed and separated with gravity and magnetism into two parts, one with iron oxide and the other with nonferrous metals such as copper, nickel, tin, etc. The former with iron oxide as a primary content can be recycled for steelmaking and the latter is recovered separately for each metal resource. Therefore the industrial contribution by this invention is significant.

Description of Figures

Figure 1 is a graph showing how much the thickness of the oxidized layer on the sheet metal depends upon the temperature when the sheet metal was oxidized with steam for 20 hours.

Figure 2 is a schematic drawing of a fixed-bed reactor used for the demonstration of this invention.

Figure 3 is a schematic drawing of a shaft-furnace reactor used for the demonstration of this invention.

Description of Legends

1: scraps
2: steam
3: gas(es) produced in this process
4: tuyere
5: refractory
6: high-frequency coil
7: scraper
8: discharge outlet

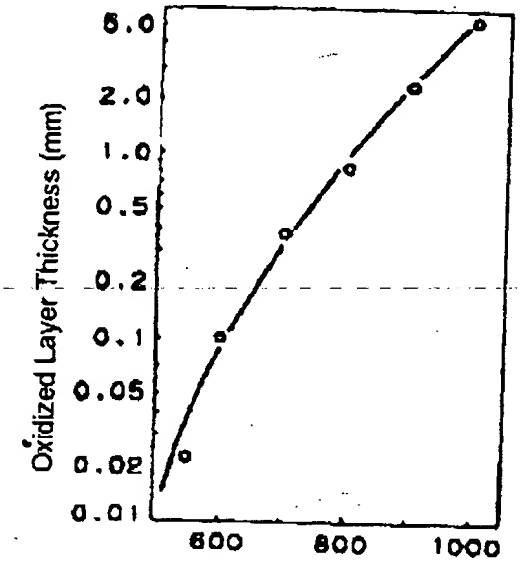


Figure 1

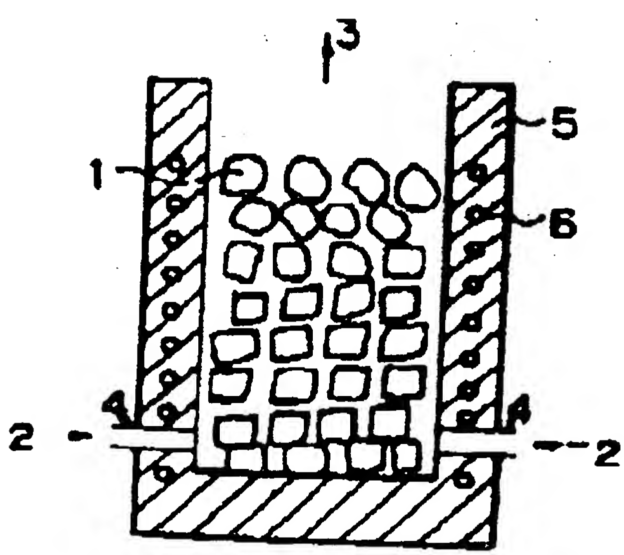


Figure 2

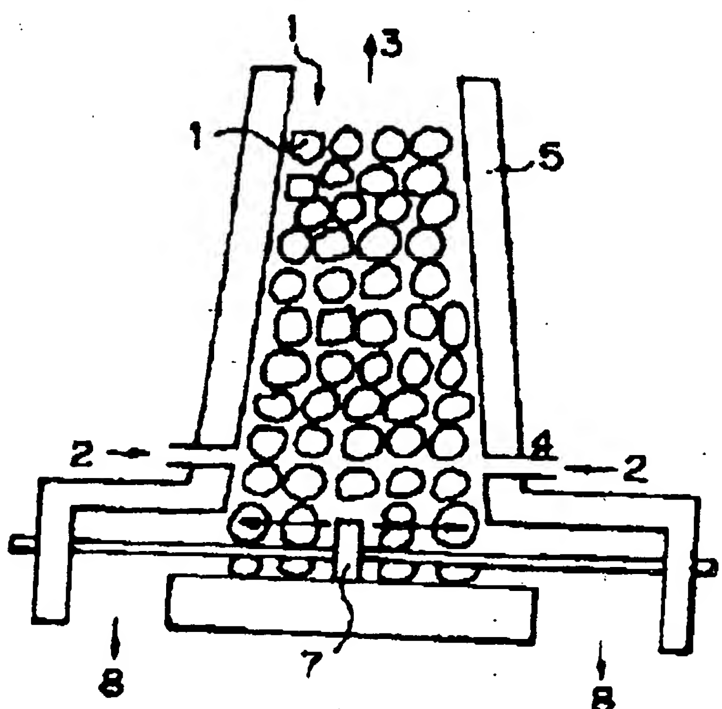


Figure 3